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An Alternative Model for Electron Correlation in Pu

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Disclaimer

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Overview of Talk

- Motivation: Pu Electronic Structure Remains Undefined
- Historical Background: Previous Models of Electron Correlation in Pu
- Historical Background: Pu Electronic Structure
- Historical background: Past Successes of DFT with Pu
- Alternative Model of Electron Correlation in Pu
- Comparison of Simulated and Experimental Spectra (Spin-Integrated)
- Remaining Problem …
- Electron Correlation Measurementsof Ce with Fano PES
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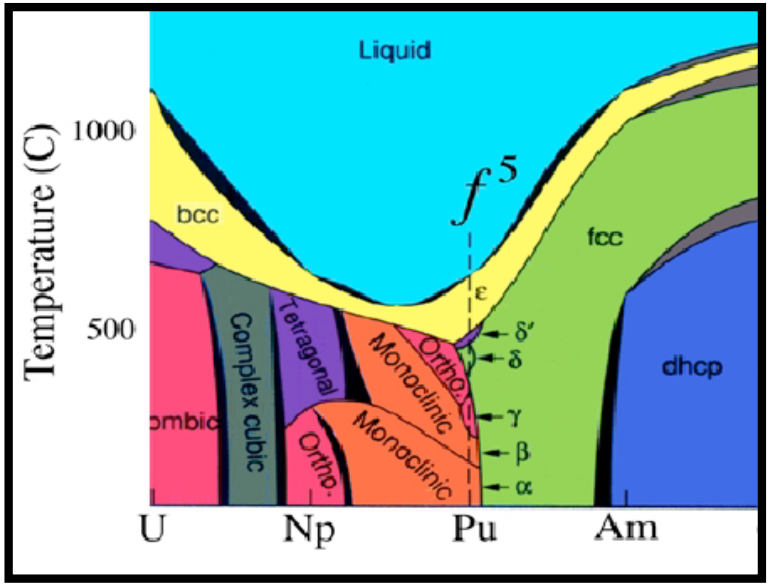
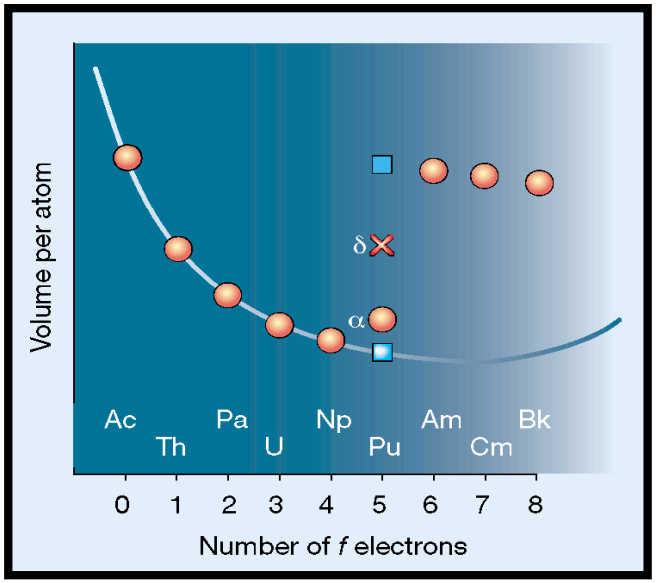
- Fano Results for the Surrogate System Pt
- Fano Simulation for Pu
- Comparison to the other models: Fano
- Future Plans
- Summary

Motivation: Pu Electronic Structure Remains Undefined

Actinide Binary Phase Diagram
Phil Mag 84,1039 (2004) and ref therein



Actinide Atomic Volumes
Albers, Nature 2003

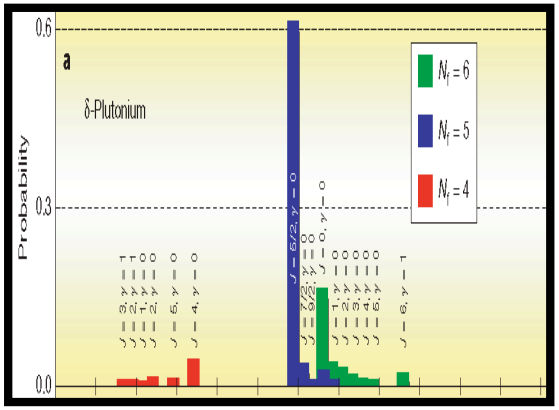


Problem: Pu is on the razor's edge

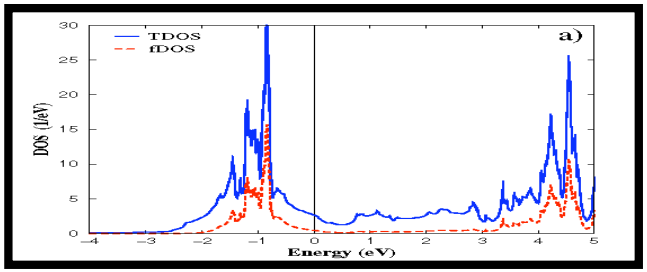
- 6 solid phases plus the liquid, at the minimum of the Binary Phase Diagram
- There is a 25% density variation between α and δ!
- Pu has schizophrenic electrons, lying between the dominance of delocalization in the light actinides (bandwidth, W) and electron correlation in the heavy actinides (coulombic repulsion,Hubbard U).

Historical background: Previous Models of Electron Correlation in Pu

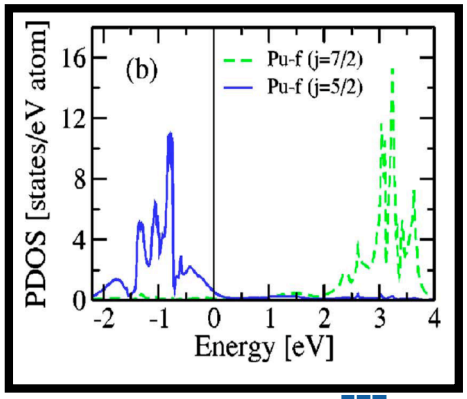
- DMFT Model: Fluctuating Valence
- Shim, Haule, and Kotliar, Nature 446, 513 (2007).
- Savrasov, Kotliar, Abrahams, Nature 410, 793(2001)



- AMF-LSDA + U w/ & w/o DMFT
- Shick, Drchal and Havela, EPL 69, 588 (2005).
- Pourovskii, Katsnelson, Lichenstein, Havela, Gouder, Wastin, Shick, Drchal and Lander, EPL 74, 479 (2006).



- LDA + U + SO
- Shorikov, Lukoyanov, Korotin, and Anisimov, PRB 72, 024458 (2005).



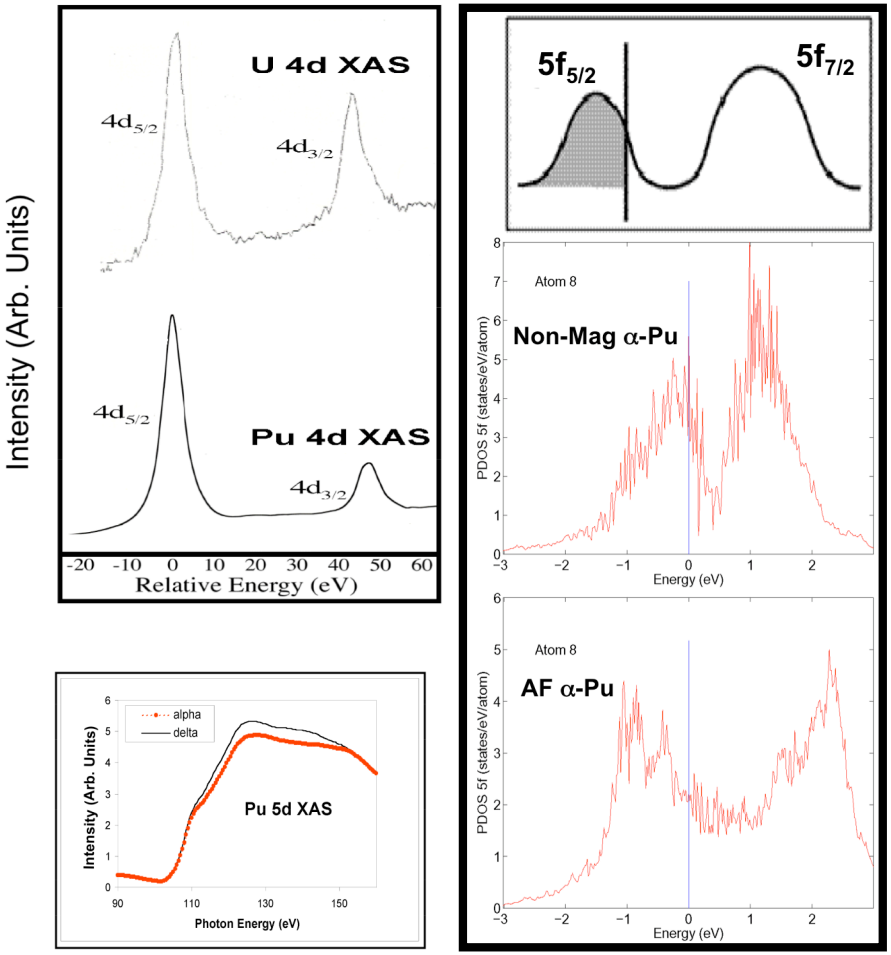
Historical Background: Pu Electronic Structure

From past studies, we know three key facts about Pu Electronic Structure…

1. **5f Spin Orbit Coupling is large**
   Branching ratios of Pu 4d XAS spectra.
   G. van der Laan et al, Phys. Rev. Lett. 93, 097401 (2004) and J.G. Tobin et al, J. Phys. Cond. Matter 20, 125204 (2008) and references therein.

2. **The number of 5f electrons is about 5**
   No pre-peak in Pu 5d XAS spectra.
   J.G. Tobin et al, J. Phys. Cond. Matter 20, 125204 (2008) and references therein.

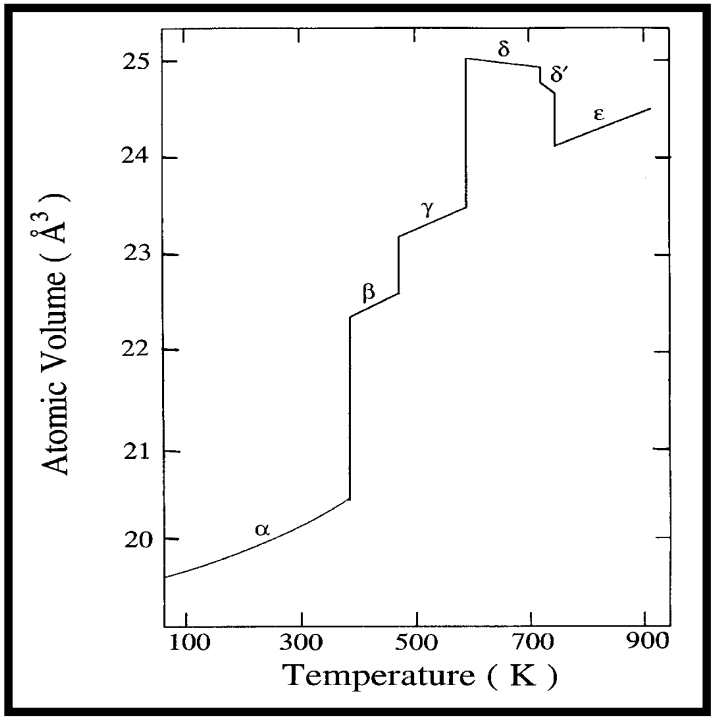
3. **Itineracy is limited in Pu:**
   $V_{SO} > V_{Delocalization}$
   Two lobes in the 5f pDOS.
   J.G. Tobin et al, Phys. Rev. B, 72 085109 (2005) and references therein.



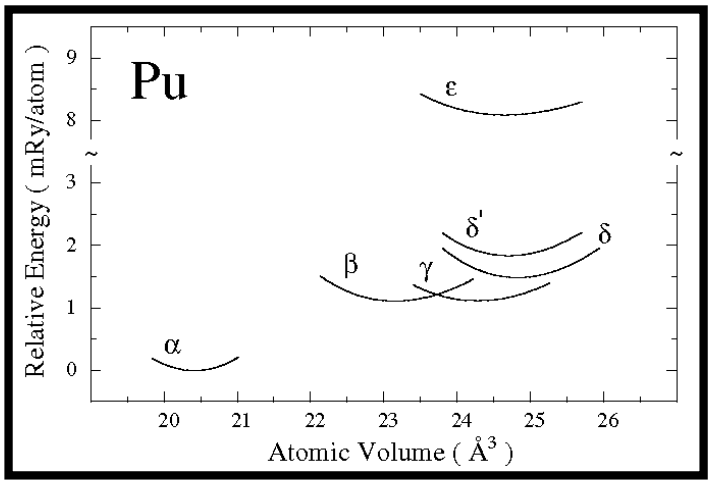
Historical Background: Past Successes of DFT with Pu

- **Using a Density Functional Approach, all six phases of Pu can be accurately predicted**
- **Söderlnd and Sadigh, PRB 92, 185702 (2004)**

Experimental Phase Diagram of Pu



Calculated Total Energies of Pu

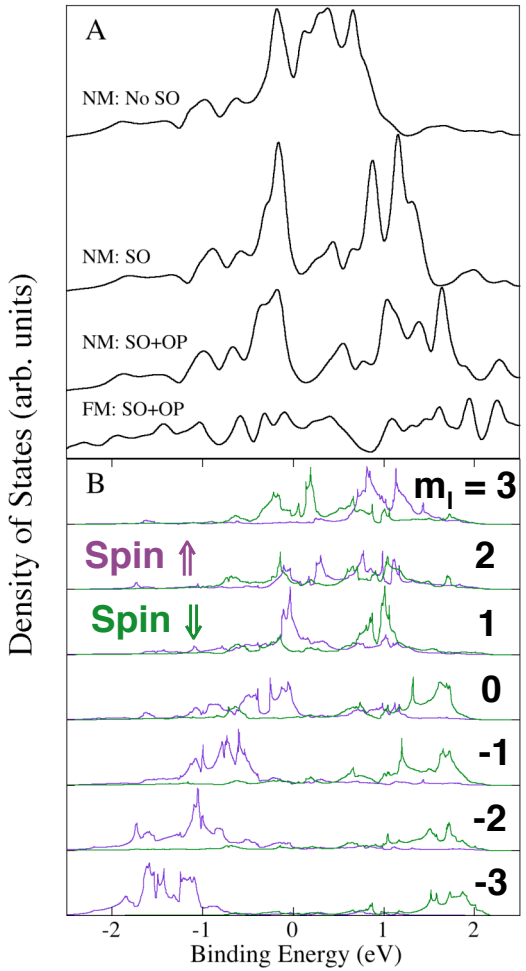


One problem remained…the magnetic moments…but we can fix that!

Our Alternative Model of Electron Correlation in Pu

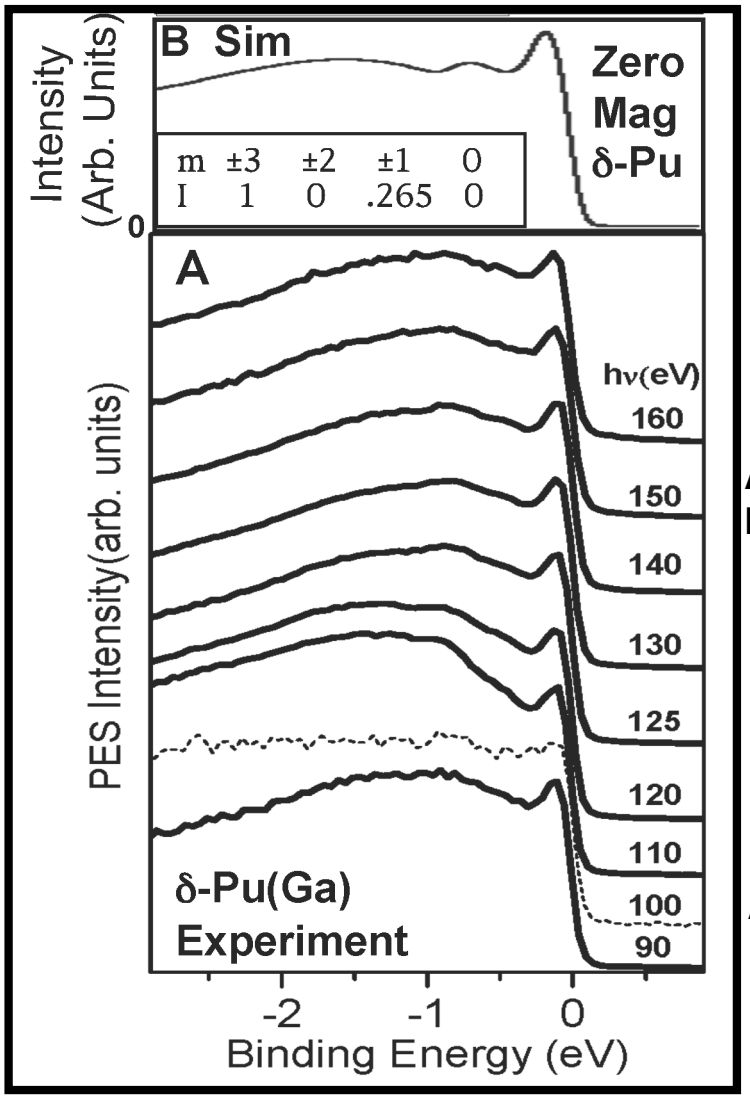
- **Start with a Density Functional Theory approach that treats the 5f electrons relativistically, and includes, itineracy, hybridization, electron spin, spin-orbit (SO) splitting and orbital polarization(OP)… Söderlind, PRB 77, 085101 (2008).**
- **Some examples are shown in Panel A, with NM = non-magnetic and FM = ferromagnetic.**
- **The result of this initial calculation for δ-Pu is almost magnetically cancelled.**
- **By reducing the 5f spin moment by only 0.35 μ_B, perfect cancellation between the 5f spin moment and the 5f orbital moment is achieved,**

  μ(5f-spin) = - μ(5f-orbital)
- **The results are shown in Panel B.**



We can test this experimentally…

Testing the Alternative Model: Comparison to PES of δ-Pu(Ga)



Above Resonance

On Res

Anti-Res

Below Res

- **Spectral Simulation: Comparison to spin-integrated of δ-Pu(Ga).**
- **Experimental spectra from Tobin et al, PRB 68, 155109 (2003).**
- **Electric dipole state-to-state transition moments (B inset) from Tobin, J. Alloys Cmpds 444-445, 154 (2007).**
- **This is NOT a comparison to DOS.**

The simulation (B) reconstructs the spectral structure (A) observed below resonance, on resonance and above resonance!

Remaining Problem: How to differentiate between the DFT Mag = 0 Model and the Fluctuating Valence DMFT Model of Kotliar et al.

- The underlying question is the following: what is the nature of the shielding?
- In DMFT, the shielding is Kondo-like, with electrons associated with the pseudo-particle peak (Kondo peak, possibly spd character) shielding the electrons associated with the Lower Hubbard Band, generally of f character.
- In the DFT Mag = 0 Model, the spin and orbital moments of the 5f states cancel out each other… μ(5f-spin) = - μ(5f-orbital).
- To differentiate between the two models, a probe must be used which is sensitive to spin polarization, fast enough to see through the shielding and not require long range magnetic ordering.
- This probe is FANO SPECTROSCOPY.

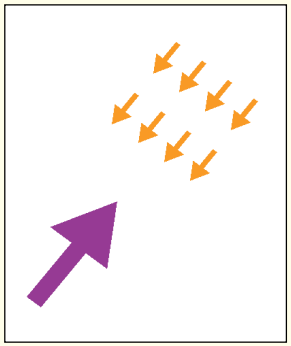
We have demonstrated how Fano Spectroscopy can probe electron correlation in a surrogate system, Ce.

The first true proof of spin shielding in a Kondo System

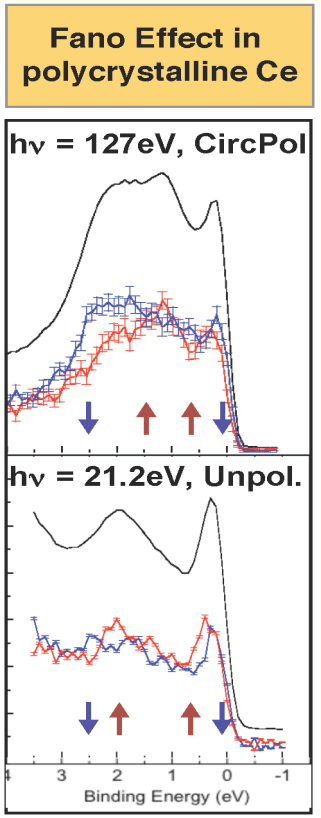
- Using spin-resolved PES of non-magnetic Ce, reversed phases are observed between the Lower Hubbard Band (LHB, BE = 2 eV, ↓↑) and the Quasiparticle Peak (QP, BE = 0 eV, ↑↓)
- The Fano Effect or Double Polarization Photoelectron Dichroism is the ideal technique with which to probe for such a dynamically shielded moment, with (1) a probe time on the scale of 10^{-15} to 10^{-18} seconds and (2) the capability to see spin effects in nonmagnetic materials!!

J.G. Tobin et al , EuroPhysics Letters (EPL) 77, 17004 (2007).

Proof of Spin Shielding in Ce



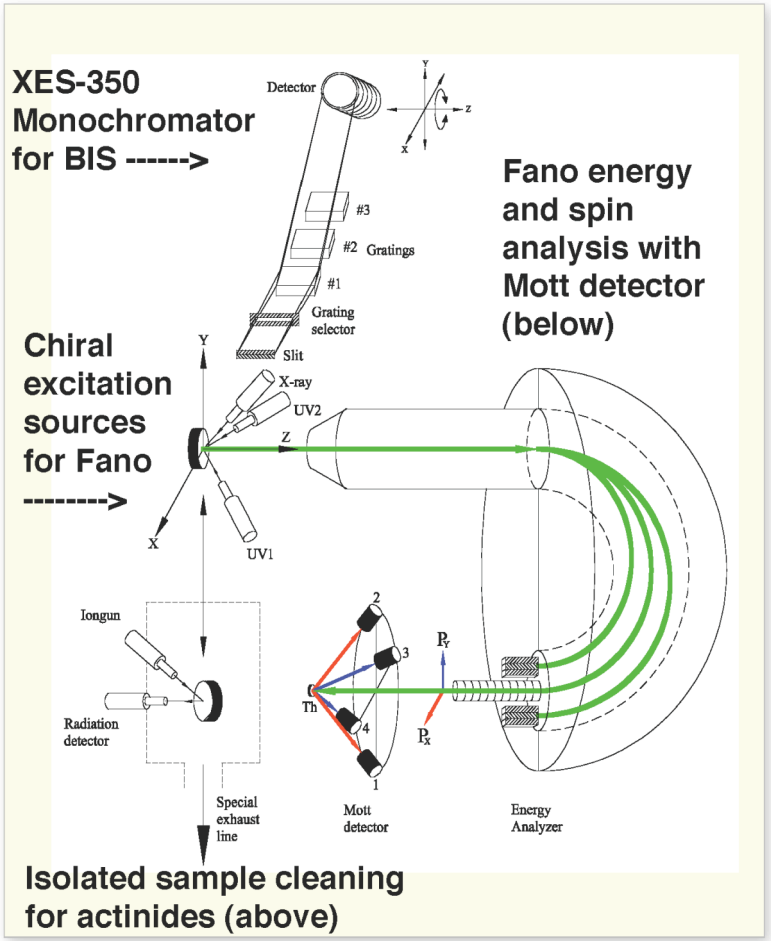
An Interpretation of Kondo Shielding and the Gunnarsson-Shoenhammer Model
The spins of the QP electrons ↑ collectively shield the spin of the LHB ↑ electron. This is a dynamic process, with zero net mag moment on the Ce.



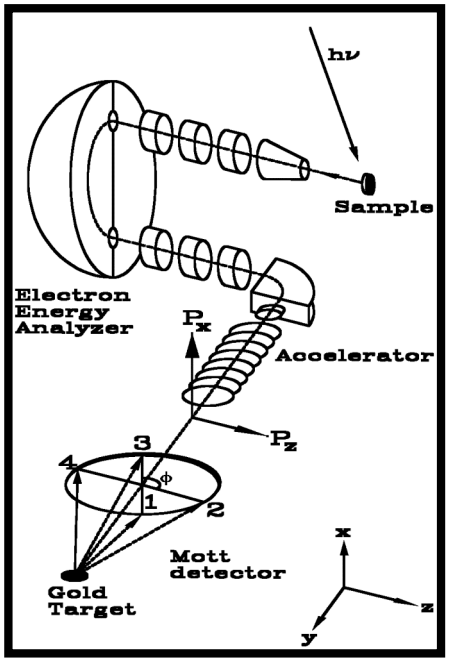
These data cannot be obtained in any other way

Digression: Experimental Capabilities for Fano Measurements

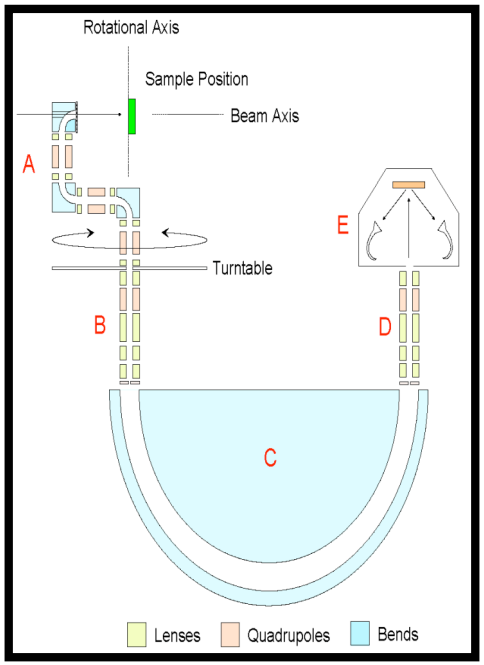
LLNL Fano and BIS Spectrometer



- We have three spin resolving spectrometers, which have been used at LLNL, the ALS/LBNL (Berkeley) and the APS/ANL(Chicago)

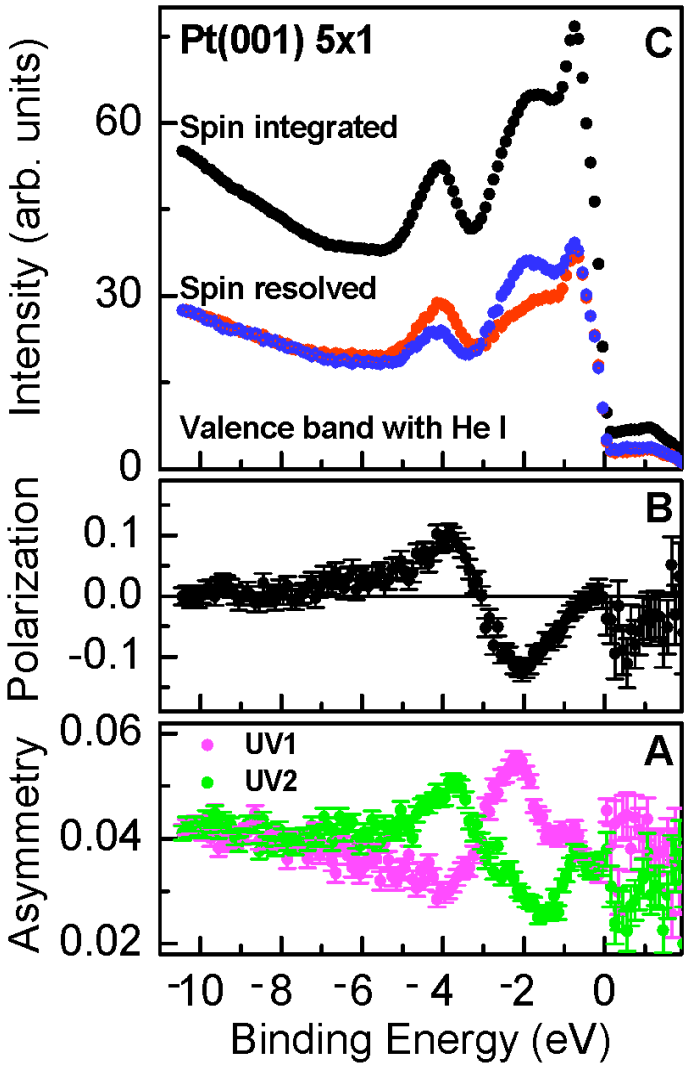


Spin Spectrometer
NIM 2007



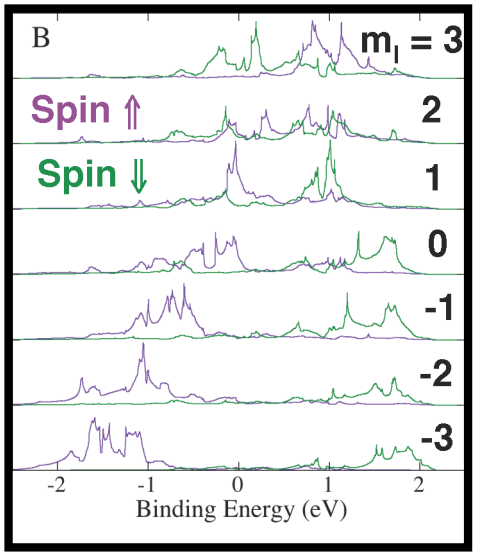
UMR Spectrometer
NIM 2007

Why should Fano Measurements work on Pu?

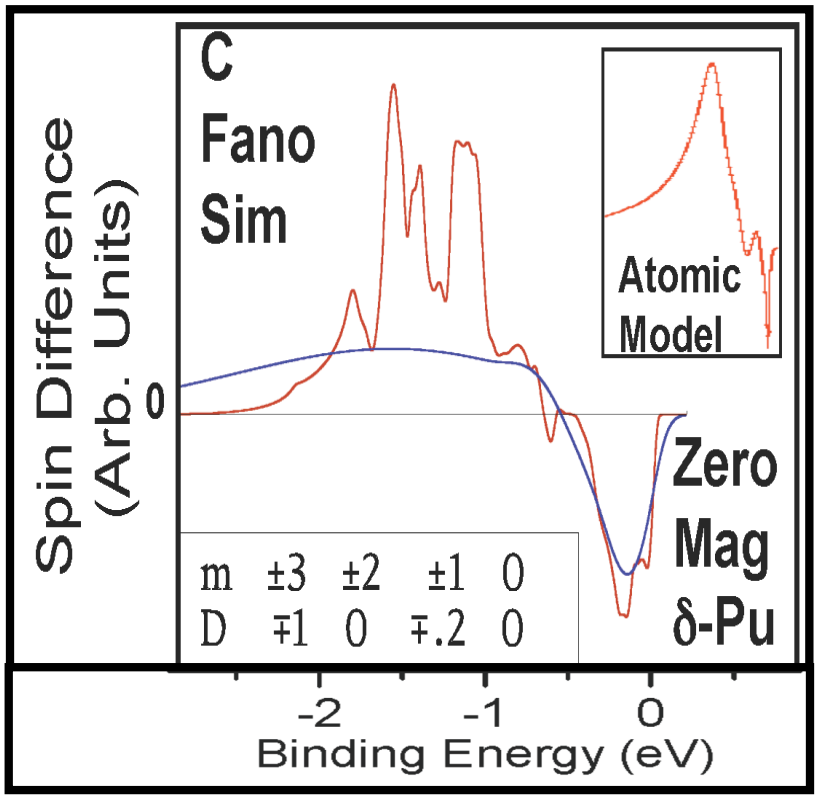


- Although we have not yet been able to perform the Pu Fano Measurements, we have done an extensive study of the surrogate system Pt… Yu and Tobin, Surface Science Letters 2007.
- Both have highly relativistic valence bands (Pu-5f, Pt-5d), which are partially occupied and have sufficient itineracy that there is 5f/5d character at the Fermi Energy.
- These measurements were made with a chiral configuration of vectors, not circularly polarized photons. In fact, the HeI sources are unpolarized and the chirality is reversed by switching from Source UV1 to UV2 (panel A), as illustrated on the previous page.
- Thus, synchrotron radiation is not necessary.
- In fact, the experiment gets easier for Pu that Ce: Pu has five 5f electrons while Ce only has one 4f electron.

Fano Simulation for Pu from the DFT Mag = 0 Model



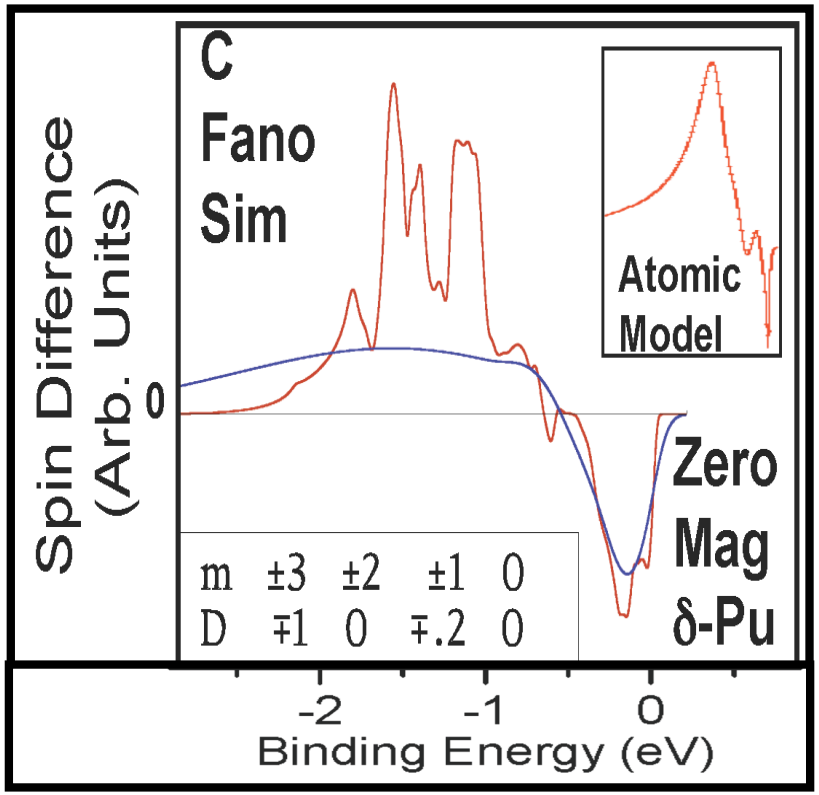
To the right: Red- without lifetime broadening Blue -with lifetime broadening



- **Spectral Simulation:**
  Spin up minus spin down.
- **Again, we start with the m_l and m_s specific states of the DFT calculation with Mag =0.**
- **Electric dipole state-to-state transition moments (C lower inset) from Tobin, J. Alloys Cmpds 444-445, 154 (2007).**
- **Fair agreement with earlier estimate using an atomic model (C upper inset, Tobin, J. Alloys Cmpds 444-445, 154 (2007)).**
- **This is NOT a comparison to DOS.**

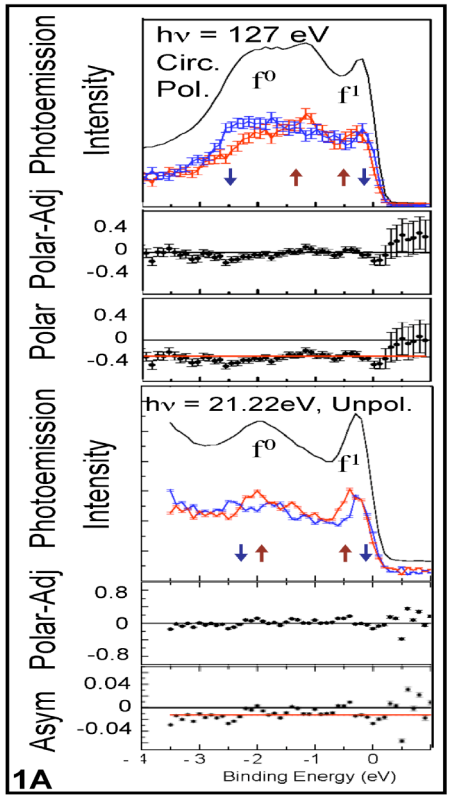
How does the DFT Mag = 0 result compare to the DMFT result?

DFT Mag = 0



- We don't really know, because those results are not available.
- But the DMFT result might look something like Ce…

Ce Fano Exp

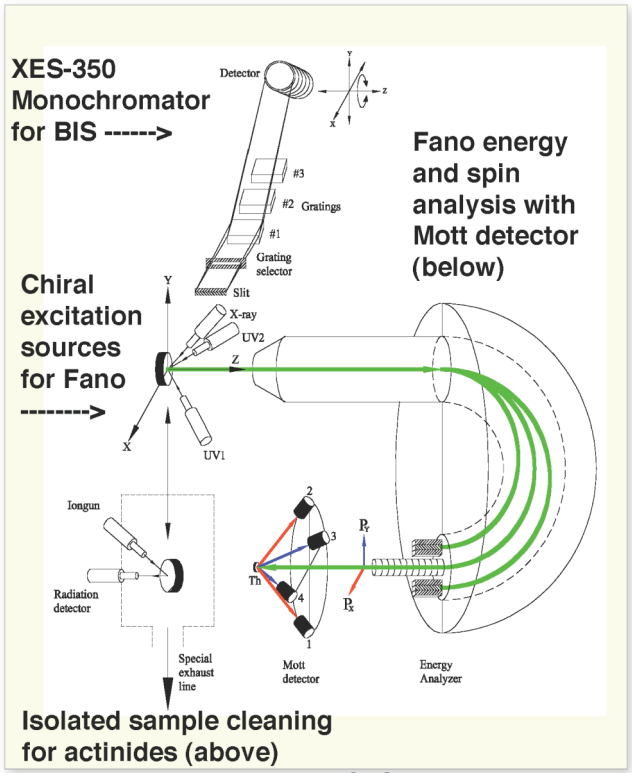


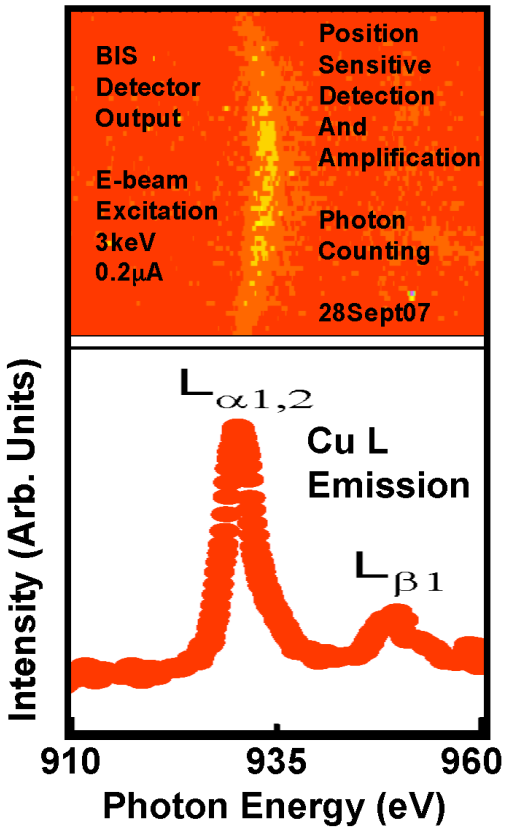
This strongly suggests that the Fano experiment should be able to differentiate between the two models!

Future Plans

Begin Fano and BIS measurements of the actinides, starting with U and URu_2Si_2 (with Jason Jeffries and Brian Maple) and moving to Pu.

LLNL Fano and BIS Spectrometer





Yu, Tobin, Söderlind…An Alternative Model

Summary

- Using a Density Functional Theory approach that treats the 5f electrons relativistically, and includes, itineracy, hybridization, electron spin, spin-orbit (SO) splitting and orbital polarization(OP) and by reducing the 5f spin moment by only 0.35 μ_B, perfect cancellation between the 5f spin moment and the 5f orbital moment is achieved,

  μ(5f-spin) = - μ(5f-orbital)

- Spectral simulations were then generated using electric dilpole transition rules and moments.
- The predictions of this model were then tested by comparing spectral simulations to the measured results of spin integrated PES of Pu, with good agreement.
- Spectral simulations of the proposed Fano experiment were then also made, again using electric dilpole transition rules and moments.
- Future Plans include the pursuit of the Pu Fano experiments, which should allow the resolution of the Pu electronic Structure Controversy.